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## The Vibrational Spectra of Methyl and Methyl- $d_3$ Nitrite

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The infrared spectra of methyl and methyl- $d_3$  nitrite have been observed between 400 and 4000  $\text{cm}^{-1}$  both in the gas phase and in an argon matrix. The very strong absorptions associated with the vibrations of the ONO group have also been observed for the carbon-13 and nitrogen-15 substituted methyl nitrites, produced by the photolysis of the corresponding nitromethane isolated in solid argon. The assignment of individual bands to the *cis* and *trans* rotamers has been facilitated by studies of the relative rates of photolysis of the two species trapped in solid argon. The vibrational assignments for the two rotamers are discussed in relation to a least-squares fit of the observed vibrational frequencies to a relatively simple set of valence force potential constants.

### INTRODUCTION

Despite several studies, much remains to be learned about the vibrational spectrum of methyl nitrite. Tarte (1) attributed a characteristic doubling of the infrared absorption bands to the presence of *cis* and *trans* rotamers. With the help of low-temperature studies, he assigned five vibrational fundamentals and several combination bands and overtone absorptions of each of these two isomers. Because of possible internal hydrogen bonding for the *cis* molecule, it was presumed to be the more stable form. Additional methyl nitrite absorptions were assigned in the argon-matrix study of Brown and Pimentel (2), who noted that the *cis* compound photolyzed more readily than the *trans*. Subsequently, the vibrational assignment for all but the two torsional fundamentals of each species, presumed to lie below 220  $\text{cm}^{-1}$ , was completed by Lippincott and co-workers (3), who studied methyl nitrite not only in the gas phase, but also in solution and in the solid state. Arguments were presented suggesting that the *trans* rather than the *cis* isomer was the more stable form, leading to a reversal in the previous assignments. However, microwave studies in the laboratory of Gwinn (4) indicated that, as originally proposed, the *cis* structure is more stable, and a recent detailed microwave study by Turner and co-workers (5) has established the structures of both isomers and an energy difference of 275  $\text{cm}^{-1}$  between them. The staggered *cis* conformation, with the two out-of-plane H atoms closest to the end O atom, is more stable than the eclipsed *cis* conformation, in which the planar H atom can hydrogen bond to the end O atom. Very recent infrared studies in the laboratory of Gunthard (6, 7) have refined the earlier assignment and have provided further data on the frequencies of the fundamentals which lie below 400  $\text{cm}^{-1}$ .

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In a study of the kinetics of the isomerization of methyl nitrite, Bauer (8) conducted a normal coordinate analysis for both rotamers, noting the need for vibrational data for the deuterated molecules. The only experimental data which have been reported for methyl- $d_3$  nitrite are those contained in a briefly communicated argon-matrix study by Ogilvie (9), who suggested assignments for six fundamentals each of the two isomers, and a report by Hartford (10) of the gas-phase spectrum between 700 and 1100  $\text{cm}^{-1}$ . A more detailed characterization of the vibrational spectra of methyl and methyl- $d_3$  nitrite would facilitate analysis of the problem of intramolecular energy transfer, addressed by Bauer (8), and of the details of the infrared multiphoton decomposition of these molecules, which are potential sources of the  $\text{CH}_3\text{O}$  reaction intermediate. The results of such a study, including both gas-phase and argon-matrix observations and a normal coordinate analysis, are presented in the following discussion.

#### EXPERIMENTAL DETAILS<sup>2</sup>

The procedures used for the synthesis and purification of methyl and methyl- $d_3$  nitrite were similar to those reported by Sanders (11). In the synthesis of methyl- $d_3$  nitrite,  $\text{D}_2\text{O}$  was used as the solvent and all reagents except the nitrosyl sulfuric acid were fully deuterated. The infrared spectra of the resulting samples showed no extraneous absorptions.

The gas-phase infrared spectra of methyl and methyl- $d_3$  nitrite between 500 and 3850  $\text{cm}^{-1}$  were obtained at 1- $\text{cm}^{-1}$  resolution using a Nicolet 7199 Fourier-transform infrared spectrometer. Both molecules were studied in a 5-cm cell at a pressure of 20 Torr.

Gas samples with an  $\text{Ar}:\text{CH}_3\text{ONO}$  (or  $\text{CD}_3\text{ONO}$ ) mole ratio of 200 were prepared by direct sampling at a pressure of approximately 4 Torr and addition of approximately 800 Torr of argon. Supplementary experiments were also conducted on nitromethane- $^{13}\text{C}$  (Merck, Sharp & Dohme of Canada, Ltd.) and nitromethane- $^{15}\text{N}$  (Prochem) samples mixed with argon to a similar mole ratio. Using cryogenic equipment and procedures which have previously been described (12), these samples were deposited at 14 K. The infrared spectra between 400 and 4000  $\text{cm}^{-1}$  of the resulting solid films were recorded using a Beckman IR-9 infrared spectrophotometer. Under the scanning conditions typical of these experiments, the resolution and relative and absolute frequency accuracies are estimated to be 1  $\text{cm}^{-1}$  between 400 and 2000  $\text{cm}^{-1}$  and 2  $\text{cm}^{-1}$  between 2000 and 4000  $\text{cm}^{-1}$ . To facilitate assignment of absorptions to the two rotamers, the deposits were then subjected to the full or filtered radiation of a medium-pressure mercury arc and the infrared spectrum again recorded. In the nitromethane studies, infrared absorptions of methyl nitrite appeared after photolysis.

#### RESULTS AND DISCUSSION

A survey spectrum of gas-phase methyl nitrite has previously been reported (13). The most prominent absorption regions for a similar sample are shown in greater

<sup>2</sup> Certain commercial instruments and materials are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the instruments or materials identified are necessarily the best available for the purpose.

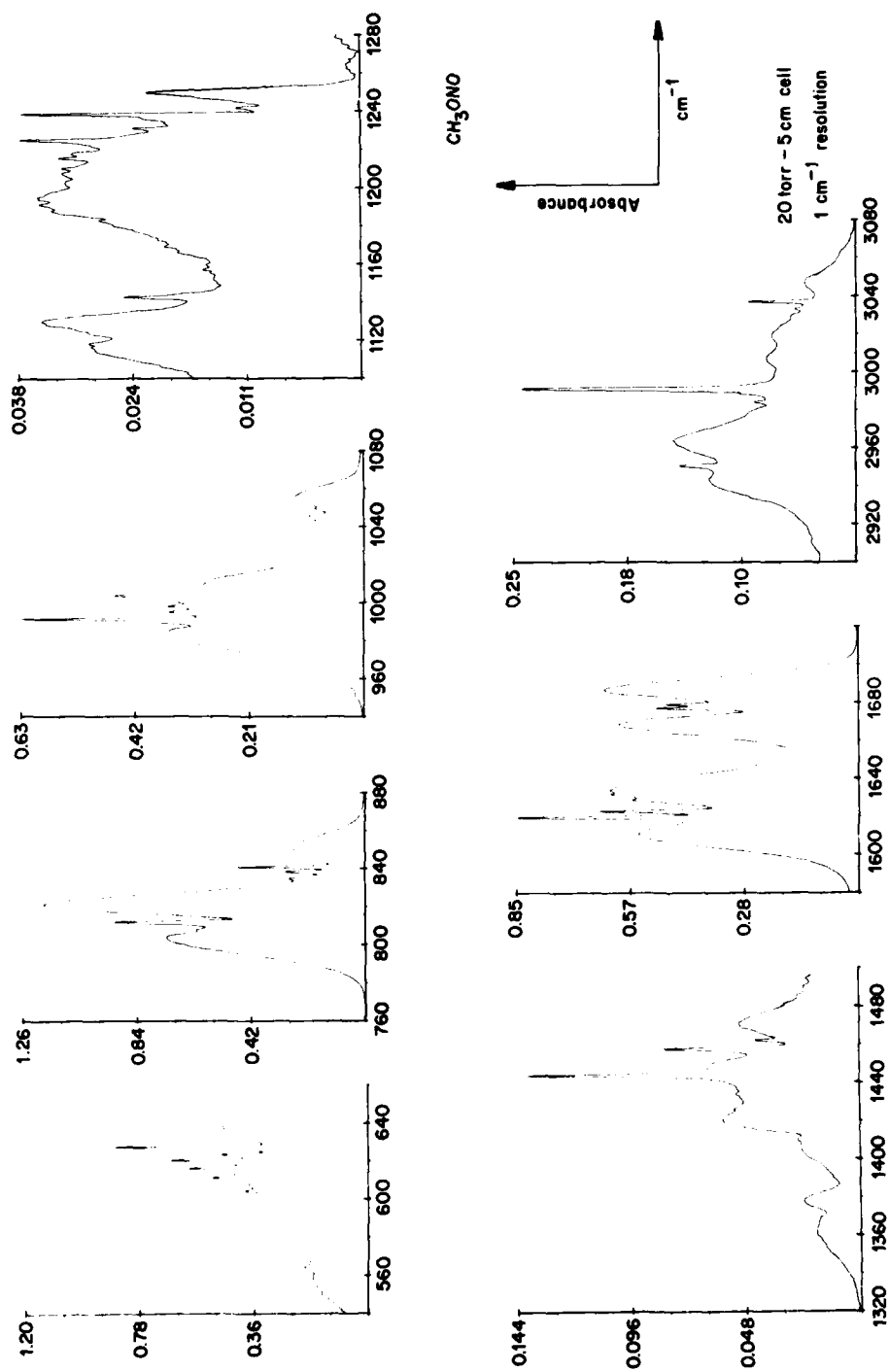
FIG. 1. Absorption Bands of  $\text{CH}_3\text{ONO}$  in the Gas Phase: 20 Torr in 5-cm cell, 1- $\text{cm}^{-1}$  resolution.

TABLE I  
Positions ( $\text{cm}^{-1}$ ) and Relative Photolysis Rates of  $\text{CH}_3\text{ONO}$  Absorptions

Gas	Ar	Rate	Assignment	Gas	Ar	Rate	Assignment
564	565	slow	trans	1420	1426	slow	trans
624	624	fast	cis	1444	1440	fast	cis
812	809	slow	trans		1449	slow	trans
833	839	fast	cis	1458	1456	fast	cis
985	987	fast	cis		1468	slow	trans
995	994	fast	cis	1620	1617	fast	cis
1046	1043	slow	trans	1677	1666	slow	trans
	1119	slow	trans 2(565)		2913	slow	trans
	1181	slow	trans	2951	2953	med	cis, trans
1239	1234	fast	cis	2994	3003	med	cis, trans
1361	1365	slow	trans 565 + 812	3037	3032	fast	cis
	1409	fast	cis		3202	fast	cis 2(1617)
					3302	slow	trans 2(1666)

detail in Fig. 1, and the estimated positions of the band centers are summarized in the first column of Table I.

The spectrum of methyl nitrite isolated in an argon matrix is shown in the solid trace of Fig. 2, and the positions of the absorption peaks in this study are summarized in the second column of Table I. The peaks characteristic of the argon-matrix studies generally lie within a few wavenumbers of the gas-phase band centers. The sharpness of the absorptions in argon-matrix observations permits the resolution of overlapping bands in the  $1400\text{--}1460\text{ cm}^{-1}$  spectral region.

The spectrum of the same sample of methyl nitrite after 64 min of photolysis by mercury-arc radiation of wavelength longer than 300 nm is shown in the broken-line trace of Fig. 2. It is evident that one of the isomers of methyl nitrite photolyzes much more readily than the other, permitting assignment of the absorptions even in the complicated  $1400\text{--}1460\text{ cm}^{-1}$  spectral region. Prominent absorptions of  $\text{H}_2\text{CO}$  and of  $\text{HNO}$  (14) also appear in the spectrum of the photolyzed sample. Further detail on the studies of photolyzed methyl nitrite is considered in a separate publication (15). The relative rates of change of the two sets of absorptions on photolysis of the sample are summarized in Table I. The resulting assignments of absorptions to the two rotamers of methyl nitrite are in agreement with but considerably extend those of Brown and Pimentel (2), who reported only the most prominent absorptions, recorded at a considerably lower resolution.

Except in the CH-stretching region, the assignment of individual peaks to the two rotamers generally also parallels that of Gunthard and co-workers (6, 7). Only two prominent absorptions, at  $2953$  and  $3003\text{ cm}^{-1}$ , appeared in this region. Severe overlapping in this region of the gas-phase spectrum led Gunthard and co-workers

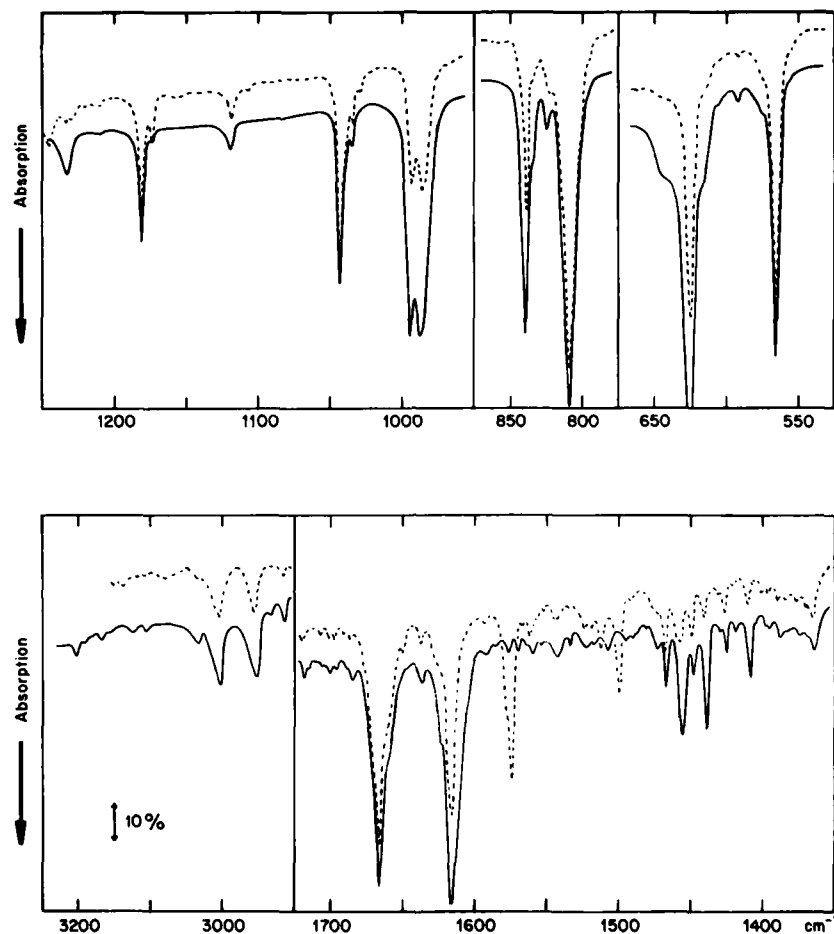


FIG. 2. —, 3.00 mmol Ar:CH<sub>3</sub>ONO = 200 deposited at 14 K without photolysis. ---, 64 min subsequent mercury-arc photolysis,  $\lambda > 300$  nm.

to base their assignment on the dependence of the intensities of the absorptions on the temperature of the deposition beam in their matrix experiments. Both of these peaks, as well as that at  $3032\text{ cm}^{-1}$ , were assigned to the *cis* rotamer. On the other hand, the three peaks which they assigned to the CH-stretching fundamentals of the *trans* rotamer were all weak or very weak and in the  $2820\text{--}2920\text{ cm}^{-1}$  spectral region. To clarify the assignment of the CH-stretching absorptions, an experiment was conducted in which the peak optical densities of the methyl nitrite absorptions between  $2900$  and  $3310\text{ cm}^{-1}$  were studied as a function of duration of photolysis by mercury-arc radiation of wavelength longer than  $345\text{ nm}$ . The assignment of the peaks at  $3032$  and  $3200\text{ cm}^{-1}$  to the *cis* rotamer and of the peaks at  $2914$  and

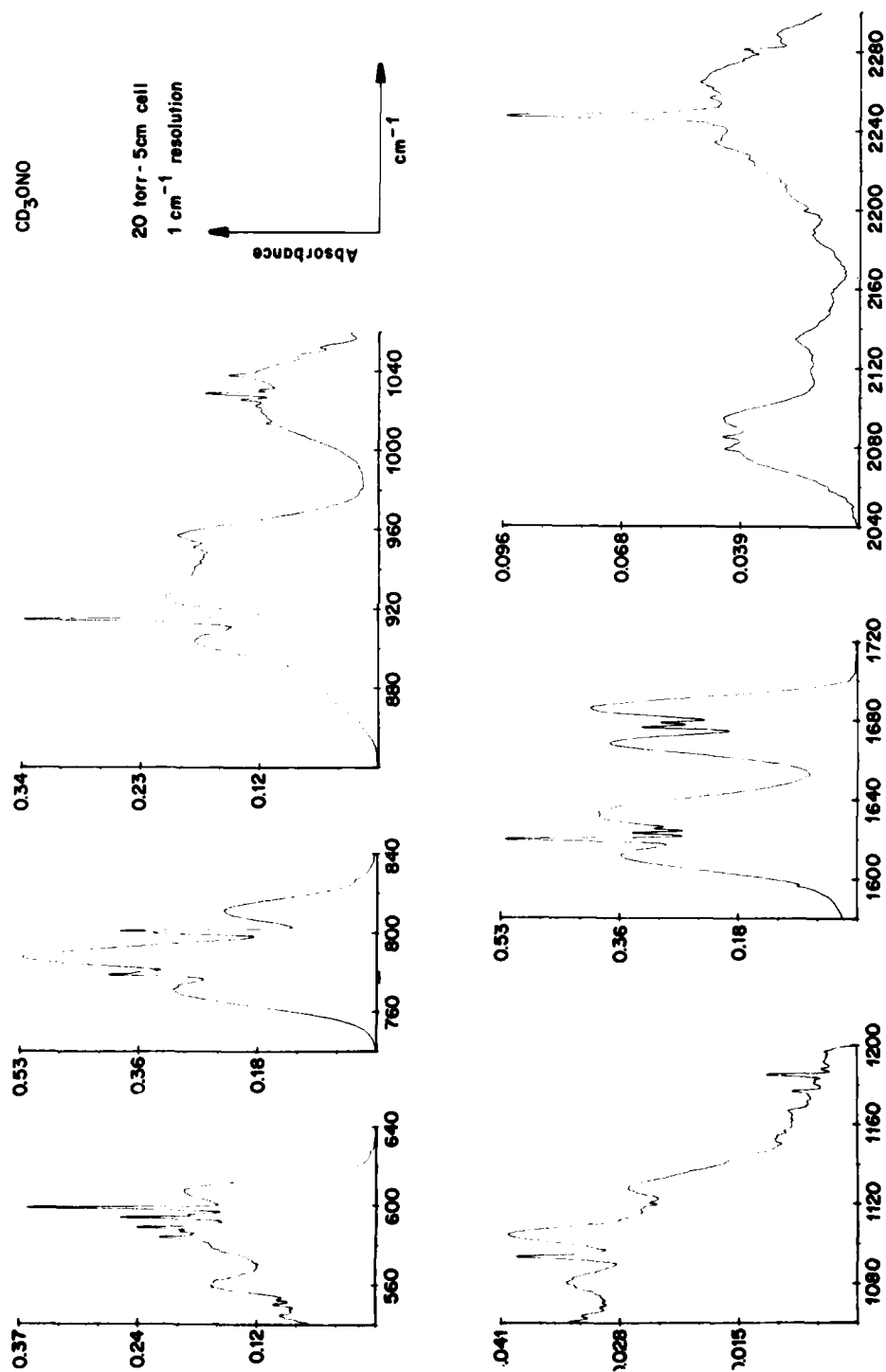


FIG. 3. Absorption Bands of CD<sub>3</sub>ONO in the gas phase: 20 Torr in 5-cm cell, 1-cm<sup>-1</sup> resolution.

TABLE II  
Positions ( $\text{cm}^{-1}$ ) and Relative Photolysis Rates of  $\text{CD}_3\text{ONO}$  Absorptions

Gas	Ar	Rate	Assignment	Gas	Ar	Rate	Assignment
550	552	slow	trans		1593	slow	trans ?
595	596	fast	cis		1597	fast	cis 2(799)
779	777	slow	trans	1619	1616	fast	cis
801	799	fast	cis	1676	1667	slow	trans
	895	fast	cis 596 + 304?	2085	2083		
915	912	fast	cis		2114		
951	949	slow	trans	2135	2126	fast	cis
	1020	slow	trans		2143		
1028	1028	fast	cis	2189	2192		
1038	1049	fast	cis		2221		
	1055	fast	cis	2233	2231		
1093	1089	fast	cis	2247	2256	fast	cis
	1093	slow	trans		2262	slow	trans
	1115	slow	trans	2281	2279	fast	cis
1185	1181	fast	cis 2(596)		2443	slow	trans 1667 + 777
1323	1322	slow	trans 777 + 552		3194	fast	cis 2(1616)
	1391	fast	cis 799 + 596		3303	slow	trans 2(1667)
	1493	slow	trans				

$3302\text{ cm}^{-1}$  to the *trans* rotamer was confirmed. However, the rates of decrease in the  $2953\text{-cm}^{-1}$  and  $3003\text{-cm}^{-1}$  absorptions were intermediate between those of the *cis* and *trans* rotamers, suggesting the possibility that both species may contribute to these absorptions.

A survey spectrum of gas-phase methyl- $d_3$  nitrite has also recently been reported (13). The most prominent absorption bands of a similar sample are shown in Fig. 3, and the estimated positions of the band centers are summarized in the first column of Table II. The corresponding spectra of methyl- $d_3$  nitrite isolated in an argon matrix before photolysis and after a 75-min exposure of the deposit to mercury-arc radiation of wavelength longer than  $345\text{ nm}$  are shown in the solid and broken-line traces, respectively, of Fig. 4. Several prominent absorptions of  $\text{D}_2\text{CO}$  and of  $\text{DNO}$  (14) appear in the spectrum of the photolyzed sample but will be discussed in a subsequent paper (15). The data obtained in the argon-matrix experiments and the proposed assignment of the absorptions to the two rotamers of  $\text{CD}_3\text{ONO}$  are also summarized in Table II. The detailed assignment in the  $2100\text{-}2200\text{ cm}^{-1}$  spectral region is complicated by the growth on photolysis of prominent absorptions of  $\text{D}_2\text{CO}$ .

Except that the frequencies of the methyl- $d_3$  nitrite absorptions in the present studies were consistently slightly higher than those reported by Ogilvie (9), the results of the two studies were generally in agreement. Just as the highest frequency



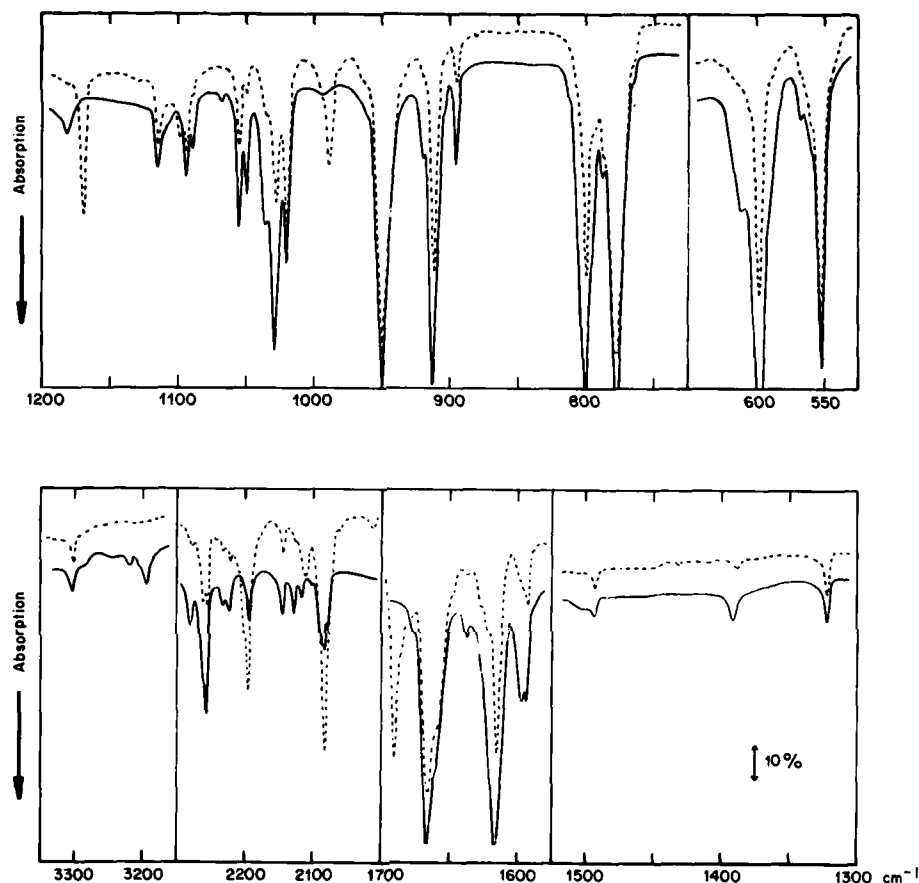


FIG. 4. —, 3.21 mmol Ar:CD<sub>3</sub>ONO = 200 deposited at 14 K without photolysis. ---, 75 min subsequent mercury-arc photolysis,  $\lambda > 345$  nm.

peak in the spectrum of the undeuterated molecule, at  $3032\text{ cm}^{-1}$ , could be assigned to the *cis* rotamer, the highest frequency peak in the CD-stretching region, at  $2279\text{ cm}^{-1}$ , is also contributed by the *cis* rotamer. By analogy with the assignment proposed by Gunthard and co-workers (6, 7) for CH<sub>3</sub>ONO, the next highest frequency peak, at  $2262\text{ cm}^{-1}$ , should be contributed by the *cis* species. However, Ogilvie assigned a peak at  $2252\text{ cm}^{-1}$  to the *trans* rotamer. In the present studies, a prominent absorption appeared at  $2256\text{ cm}^{-1}$  with a shoulder at  $2262\text{ cm}^{-1}$ . As is shown in Fig. 4, when the sample was photolyzed the  $2256\text{-cm}^{-1}$  peak disappeared relatively rapidly, but its higher-frequency shoulder persisted, indicating that there is a close coincidence between the absorptions of the two rotamers and supporting the suggestion that there is also such a coincidence for the  $3003\text{-cm}^{-1}$  peak of the undeuterated molecule.

When samples of nitromethane-<sup>13</sup>C and of nitromethane-<sup>15</sup>N isolated in an argon

matrix were exposed to the full light of a medium-pressure mercury arc for 30 or 40 min, six new absorptions, readily assigned to the prominent vibrations of the ONO group of the corresponding *cis*- and *trans*-methyl nitrite, appeared. Absorptions at 625, 831, and 1611  $\text{cm}^{-1}$  were assigned to *cis*- $^{13}\text{CH}_3\text{ONO}$ , at 560, 802, and 1667  $\text{cm}^{-1}$  to *trans*- $^{13}\text{CH}_3\text{ONO}$ , at 621, 823, and 1586  $\text{cm}^{-1}$  to *cis*- $\text{CH}_3\text{O}^{15}\text{NO}$ , and at 560, 793, and 1639  $\text{cm}^{-1}$  to *trans*- $\text{CH}_3\text{O}^{15}\text{NO}$ . In the earlier study of the photolysis of matrix-isolated nitromethane by Brown and Pimentel (2) only the absorptions of *trans*-methyl nitrite were observed, because of the secondary photodecomposition of the *cis* rotamer during the relatively long photolysis period used in their experiments.

Normal coordinate analyses were conducted for both *cis*- and *trans*-methyl nitrite using the molecular structures derived from the microwave studies (5), the vibrational frequencies and assignments obtained in the experiments here reported, and the *G*-matrix and least-squares force constant adjustment programs, GMAT and FADJ, of Schachtschneider (16). Where the gas-phase band centers were identified, their frequencies, rather than those observed in an argon matrix, were used in the fit. The positions of the gas-phase band centers for the  $^{13}\text{CH}_3\text{ONO}$  and  $\text{CH}_3\text{O}^{15}\text{NO}$  absorptions were estimated by assuming that their argon-matrix shifts were the same as those of the corresponding absorptions of  $\text{CH}_3\text{ONO}$ . Because of the typically large difference between the anharmonicity of CH- and CD-stretching vibrations and the ambiguities in the possible assignments of absorptions in the CD-stretching region, frequencies in this region were not used in the force constant adjustment. Band centers for the absorptions below 400  $\text{cm}^{-1}$  were taken from the

TABLE III  
Isotopic Dependence of ONO Vibrations ( $\text{cm}^{-1}$ ) of *trans*-Methyl Nitrite

Species		$\nu_{\text{N=O}}$	$\nu_{\text{H-O}}$	$\nu_{\text{ONO}}$
$^{12}\text{CH}_3\text{O}^{14}\text{NO}$	Obs.	1677	812	564
	Calc.	1678.6	811.8	564.2
	$\Delta\nu$	-1.6	0.2	-0.2
$^{13}\text{CH}_3\text{O}^{14}\text{NO}$	Obs.	1678	805	559
	Calc.	1678.6	810.4	560.9
	$\Delta\nu$	-0.6	-5.4	-1.9
$^{12}\text{CH}_3\text{O}^{15}\text{NO}$	Obs.	1650	796	559
	Calc.	1645.9	796.0	562.6
	$\Delta\nu$	4.1	0.0	-3.6
$^{12}\text{CD}_3\text{O}^{14}\text{NO}$	Obs.	1676	779	550
	Calc.	1678.0	773.0	547.0
	$\Delta\nu$	-2.0	6.0	3.0

studies of Gunthard and co-workers (6, 7). The microwave studies of Turner and co-workers (5) have shown that the barrier to free rotation of the methyl group of *trans*-methyl nitrite is very small. Accordingly, the frequency of the methyl torsion of this molecule has been assumed to equal zero in the normal coordinate calculations. A valence force potential which included all of the principal force constants except that for the methyl torsion of *trans*-methyl nitrite and the smallest number of interaction constants for which a reasonable fit to the data could be obtained was used. A single CH-stretching force constant was assumed, and the hypothesis that the *trans*-rotamer contributes to the absorptions at 2953 and 3003  $\text{cm}^{-1}$  was tested by fitting this force constant to them. Because the CH-stretching modes are approximately separable from the rest of the problem, this assumption should affect the results for the lower frequency modes far less than should the omission of interaction constants involving these other modes. The initial force constants for the  $\text{CH}_3\text{O}$  group were estimated from the corresponding force constants calculated by Timidei and Zerbi (17) for methanol, and those for the ONO group from the force constants reported by Guillory and Hunter (18) for *cis*-HONO. The calculations for these two molecules suggested that there may be significant interaction constants between the C-O stretch and the HCO bend and between the N-O stretch and the ONO bend. The initial force constants for the torsion vibrations were estimated by assuming these vibrations to be approximately separable from those at higher frequencies.

As the calculations for *trans*-methyl nitrite proceeded, it was found to be desirable to include the interaction constant between the C-O stretch and the  $\text{CH}_2$  bending vibration. Gas-phase frequencies (or their values estimated by assuming matrix shifts for the carbon-13 and nitrogen-15 compounds similar to those for the ordinary compound) were used except for the *trans*- $\text{CH}_3\text{ONO}$  absorptions at 1468, 1449, and 1181  $\text{cm}^{-1}$  and the *trans*- $\text{CD}_3\text{ONO}$  absorptions at 1115 and 1093  $\text{cm}^{-1}$ , for which the gas-phase bands were severely overlapped or were not detected.

As is shown in Table III, the fit to the data for the ONO vibrations resulting from the least-squares force constant adjustment calculation is generally reasonable. The 5- $\text{cm}^{-1}$  deviation for the N-O stretching vibration of  $^{13}\text{CH}_3\text{ONO}$  suggests that the extent of carbon-atom motion in this vibration is underestimated.

The comparison between the observed and calculated frequencies for the other *trans*-methyl nitrite absorptions, summarized in Table IV, is also quite satisfactory, with the largest deviations associated with the CH-stretching vibrations. The 21- $\text{cm}^{-1}$  deviations for the two assigned CH-stretching vibrations could be corrected for by introducing a CH-stretching interaction force constant. Since the assignment of these two vibrations is tentative, such a correction is unwarranted. The third CH-stretching vibration was calculated to lie at 2854  $\text{cm}^{-1}$ , quite close to a moderately intense absorption at 2843  $\text{cm}^{-1}$  which Lippincott (3) assigned to a combination band but Ghosh and Gunthard (7) to a difference band. These workers have assigned a very weak absorption at 2829  $\text{cm}^{-1}$  to a CH-stretching fundamental of *trans*-methyl nitrite. Alternatively, this absorption may be contributed by the overtone of the 1420- $\text{cm}^{-1}$  fundamental. The assignment of the more prominent 2913- $\text{cm}^{-1}$  absorption as the lowest frequency CH-stretching fundamental of the *trans* species appears more reasonable, but an alternative assignment of this peak

TABLE IV  
Normal Coordinate Analysis for *trans*-Methyl Nitrite

cm <sup>-1</sup>			Potential Energy Distribution																
Obs.	Calc.	$\Delta\nu$		F <sub>CH</sub>	F <sub>N=O</sub>	F <sub>CO</sub>	F <sub>N-O</sub>	F <sub>HCH'</sub>	F <sub>HCH</sub>	F <sub>H'CO</sub>	F <sub>HCO</sub>	F <sub>CON</sub>	F <sub>ONO</sub>	F <sub>T<sub>1</sub></sub>	F <sub>HCH</sub> <sup>CO</sup>	F <sub>H'CO</sub> <sup>CO</sup>	F <sub>HCO</sub> <sup>CO</sup>	F <sub>ONO</sub> <sup>NO</sup>	
(a) CH <sub>3</sub> ONO																			
2994	2972.5	21.5	a"	99															
2951	2972.0	-21.0	a'	99															
	2853.5		a'	100															
1677	1678.6	-1.6	a'		92		2						1	3				1	
1468	1473.2	-5.2	a'					32	4	24	41					-1	-2		
1449	1444.2	4.8	a"					73			27								
1420	1418.9	1.1	a'			2		17	41	18	16				2	-2	5		
1181	1180.3	0.7	a'	1		5	2	8	30	41	7	7	2		-2	-5	5	-1	
	1171.3		a"	1				27			72								
1046	1046.7	-0.7	a'		2	93	1	3	3	2	24	2	8		-3	5	-42	2	
812	811.8	0.2	a'			6	57		1	3		11	52			-2	1	-31	
564	564.2	-0.2	a'		4	12	33				2	1	33			1	-4	18	
379	377.1	1.9	a'		1	3	13		1	1		77	10			-1	1	-7	
180	180.0	0.0	a"											100					
$\tau_2$			a"																
(b) CD <sub>3</sub> ONO																			
	2220.6		a'	98						1	1		1						
	2219.3		a"	98				1				1							
	2054.7		a'	98		2										-1			
1676	1678.0	-2.0	a'		92		2						2	3				1	
1115	1116.9	-1.9	a'	1	2	48			4	6	8	8	10		2	-7	18	-1	
1093	1089.1	3.9	a'	1		12		41	2	36	35				-1	-8	-18		
1022	1028.2	-6.2	a"					75			25								
	965.3		a'		1	22		12	65		17	2	3		-6	1	-17		
951	949.9	1.1	a'	2		21	20	5	5	28	20	7	1		2	9	-18	-3	
	911.5		a"	2				24			73								
779	773.0	6.0	a'			3	40	2	3	13	6	3	55			-2	4	-27	
550	547.0	3.0	a'		4	13	36			3	2		27			2	-5	17	
	347.2		a'		1	2	10		1	2	1	77	9			-1	1	-6	
	175.5		a"											100					
$\tau_2$			a"																
$F_j^{\dagger}$					4.69	11.62	5.07	2.63	0.49	0.44	0.89	0.92	1.38	1.77	0.088	-0.12	0.40	0.67	
uncertainty <sup>†</sup>					0.02	0.09	0.17	0.38	0.02	0.02	0.07	0.08	0.11	0.26	0.010	0.08	0.10	0.06	

<sup>†</sup> Stretching force constants,  $\times 10^2$  N m<sup>-1</sup>; bending and bending interaction force constants,  $\times 10^{-18}$  N m;  
stretch-bending interaction force constants,  $\times 10^{-8}$  N.

to the overtone of the 1468-cm<sup>-1</sup> fundamental is also possible. Typical anharmonic corrections would place the highest frequency CD-stretching vibration of *trans*-CD<sub>3</sub>ONO significantly above the calculated value of 2220 cm<sup>-1</sup>. Also considering that the calculated position of the highest frequency CH-stretching fundamental

was  $21\text{ cm}^{-1}$  below the tentatively assigned value, the correlation of the  $2262\text{-cm}^{-1}$  absorption observed for *trans*- $\text{CD}_3\text{ONO}$  with the  $2994\text{-cm}^{-1}$  absorption of *trans*- $\text{CH}_3\text{ONO}$  is straightforward. Six other absorptions in the CD-stretching region could not be definitively assigned to the *cis* or *trans* rotamer because of spectral interference by  $\text{D}_2\text{CO}$ . A  $2951\text{-cm}^{-1}$  *trans*- $\text{CH}_3\text{ONO}$  absorption would correlate quite well with the  $2231\text{-cm}^{-1}$   $\text{CD}_3\text{ONO}$  absorption, and the appearance of another  $\text{CD}_3\text{ONO}$  absorption only  $10\text{ cm}^{-1}$  lower in frequency would be consistent with the assumption that absorptions of both rotamers lie near  $2953\text{ cm}^{-1}$ . The third CD-stretching fundamental, calculated to appear near  $2055\text{ cm}^{-1}$ , can be correlated with the observed absorption at  $2085\text{ cm}^{-1}$ . Unfortunately, spectral interference from  $\text{CD}_2\text{O}$  prevents a definitive assignment of this peak to *trans*- $\text{CD}_3\text{ONO}$ . The combination band involving the  $1667\text{-}$  and  $552\text{-cm}^{-1}$  absorptions of *trans*- $\text{CD}_3\text{ONO}$  should lie near  $2219\text{ cm}^{-1}$ , and its counterpart for the *cis* rotamer should lie near  $2212\text{ cm}^{-1}$ , suggesting that either or both of the absorptions at  $2221$  and  $2192\text{ cm}^{-1}$  may be contributed by combination bands.

In the gas-phase studies of Lippincott (3), the absorptions in the  $1400\text{--}1500\text{ cm}^{-1}$  spectral region were badly overlapped. However, it was suggested that the two  $a'$  fundamentals should appear at somewhat higher frequencies than the  $a''$  fundamental. In the present calculations, the  $a''$  fundamental is intermediate in frequency, consistent with the assignment of Gunthard and co-workers (6, 7). Lippincott assigned gas-phase absorptions at  $1046$  and  $1035\text{ cm}^{-1}$  to  $a'$  and  $a''$  fundamentals, respectively. Gunthard has attributed the  $1035\text{-cm}^{-1}$  peak to methanol impurity. In an argon matrix, the shoulder at  $1035\text{ cm}^{-1}$  on the  $1043\text{-cm}^{-1}$  absorption of *trans*- $\text{CH}_3\text{ONO}$  may, alternatively, be attributed to the existence of multiple trapping sites in the solid. The calculations of Bauer (8) suggested that this fundamental should lie near  $1202\text{ cm}^{-1}$ , and the present calculations suggest a position near  $1171\text{ cm}^{-1}$ . Lippincott proposed the assignment of several moderately intense absorptions between  $1110$  and  $1150\text{ cm}^{-1}$  to combination bands. Conceivably the  $a''$  fundamental contributes one of these bands. Fundamentals of *trans*- $\text{CD}_3\text{ONO}$  having  $a''$  symmetry are calculated to lie at  $1028$  and  $911\text{ cm}^{-1}$ . A *trans*- $\text{CD}_3\text{ONO}$  absorption appears at  $1022\text{ cm}^{-1}$ , in good agreement with the calculation, but an absorption near  $911\text{ cm}^{-1}$  would be obscured by the very prominent  $915\text{-cm}^{-1}$  absorption of *cis*- $\text{CD}_3\text{ONO}$ .

The force constants obtained for *trans*- $\text{CH}_3\text{ONO}$ , summarized in Table IV, are of typical magnitude for such a molecule and, in general, have relatively small statistical uncertainties. The larger uncertainties in the CO- and N-O-stretching force constants and in the ONO-bending force constant are consistent with the large amount of mixing expected for these molecular motions. Although the fit could be refined by the addition of more interaction force constants, the relatively simple set of potential constants obtained in this calculation provides a reasonable assignment for the vibrational spectra of both *trans*- $\text{CH}_3\text{ONO}$  and *trans*- $\text{CD}_3\text{ONO}$ .

The expectation that the interaction between the CON and ONO bending motions would also be significant in the corresponding calculation for the *cis* rotamer was readily confirmed, but as the calculations were refined it was found that the interaction between the CO-stretching motion and the out-of-plane hydrogen deformation motions was much smaller than for the *trans* rotamer, and it was removed

TABLE V  
Isotopic Dependence of ONO Vibrations ( $\text{cm}^{-1}$ ) of *cis*-Methyl Nitrite

Species		$\nu_{\text{N=O}}$	$\nu_{\text{N-O}}$	$\nu_{\text{ONO}}$
$^{12}\text{CH}_3\text{O}^{14}\text{NO}$	Obs.	1620	838	624
	Calc.	1620.1	841.1	637.2
	$\Delta\nu$	-0.1	-3.1	-13.2
$^{13}\text{CH}_3\text{O}^{14}\text{NO}$	Obs.	1614	830	625
	Calc.	1620.1	835.1	635.7
	$\Delta\nu$	-6.1	-5.1	-10.7
$^{12}\text{CH}_3\text{O}^{15}\text{NO}$	Obs.	1589	822	621
	Calc.	1588.8	827.8	635.5
	$\Delta\nu$	0.2	-5.8	-14.5
$^{12}\text{CD}_3\text{O}^{14}\text{NO}$	Obs.	1619	801	595
	Calc.	1619.7	799.0	582.2
	$\Delta\nu$	-0.7	2.0	12.8

from the calculation. The interaction constant between the N-O-stretching and ONO-bending vibrations was also found to equal zero, within the uncertainty of the fit. The results of the least-squares fit of this set of force constants to the observed frequencies (again using estimated gas-phase frequencies except for the 1440-, 1409-, 995-, and 985- $\text{cm}^{-1}$  peaks of  $\text{CH}_3\text{ONO}$  and the 1049- and 1028- $\text{cm}^{-1}$  peaks of  $\text{CD}_3\text{ONO}$ , in regions complicated by severe overlapping) are summarized in Tables V and VI.

In the CH-stretching region, only the 3032- $\text{cm}^{-1}$  peak, definitively assigned to *cis*- $\text{CH}_3\text{ONO}$ , was used in the calculation. Peaks at 2126, 2256, and 2279  $\text{cm}^{-1}$  in the spectrum of  $\text{CD}_3\text{ONO}$  isolated in an argon matrix could be assigned to the *cis* molecule but were not used in the fit because of the expected large anharmonic correction. Since this correction would lead to calculated C-D stretching fundamentals somewhat below the positions of the observed absorptions, the agreement between the observed and calculated CD-stretching vibrations of *cis*- $\text{CD}_3\text{ONO}$  is reasonable.

The largest deviation from an observed absorption frequency of *cis*-methyl nitrite occurred for the 1458- $\text{cm}^{-1}$  fundamental, calculated to appear at 1501  $\text{cm}^{-1}$ . Because this vibration possesses *a'* symmetry, it can interact with the  $\text{N}=\text{O}$  stretching vibration, at 1620  $\text{cm}^{-1}$ . The significant shift in the position observed for the  $\text{N}=\text{O}$  stretching fundamental on carbon-13 substitution supports the occurrence of such a nonbonded-atom interaction.

As is indicated in Table II, four absorptions between 1025 and 1100  $\text{cm}^{-1}$  in the spectrum of  $\text{Ar}:\text{CD}_3\text{ONO}$  samples disappeared relatively rapidly on photolysis, consistent with their assignment to *cis*- $\text{CD}_3\text{ONO}$ . The proximity of the 1049- and

TABLE VI  
Normal Coordinate Analysis for *cis*-Methyl Nitrite

cm <sup>-1</sup>			Potential Energy Distribution														
Obs.	Calc.	$\Delta\nu$		$F_{CH}$	$F_{N=O}$	$F_{CO}$	$F_{N-O}$	$F_{HCH'}$	$F_{HCH}$	$F_{H'CO}$	$F_{HCO}$	$F_{CON}$	$F_{ONO}$	$F_{\tau_1}$	$F_{\tau_2}$	$F_{H'CO}^{CO}$	$F_{ONO}^{CON}$
(a) CH <sub>3</sub> ONO																	
3032	3032.1	-0.1	a'	99													
	3015.3		a''	99													
	2890.8		a'	100													
1620	1620.1	-0.1	a'		93		2						3	4			-2
1458	1801.2	-43.2	a'					37	21	40							
1440	1441.6	-1.6	a''					95			2				3		
1409	1406.3	2.7	a'		8		2	48	24	26							-9
1239	1244.8	-5.8	a'		28	7	15	8	10	16			4			11	1
995	1005.7	-10.7	a'		2	25	8	4		18	22	13	31			-14	-9
985	987.6	-2.6	a''				2			97							
838	841.1	-3.1	a'		35	38				1	2	5	18			-4	4
624	637.2	-13.2	a'		5	11	23	1		7	5	32	38			-6	-16
346	333.1	12.9	a'			3	23			1	1	51	11			-1	11
255	256.4	-1.4	a''					1						51	48		
153	150.4	2.6	a''					2						49	49		
(b) CD <sub>3</sub> ONO																	
	2273.0		a'	98					1	1							
	2246.8		a''	98				1			1						
	2076.7		a'	98		1											
1619	1619.7	-0.7	a'		93		2					3	4				-2
	1195.6		a'	1		58	8	3	8	1	16	1	9			-5	-1
1093	1095.9	-2.9	a'			1	6	30		62	3		2			-5	
1049	1045.3	3.7	a''	1				95							4		
1028	1029.9	-1.9	a'	1			5	16	64	3	2	1	4			1	1
915	893.2	21.8	a'	1	2		4	5		18	23	20	41			-2	-13
801	799.0	2.0	a'		1	32	31	1	5	1	10	11	5			1	4
	754.4		a''	1							98			1			
595	582.2	12.8	a'		4	13	25	3		13	15	14	32			-9	-10
	306.7		a'			4	18	1		3	3	54	8			-2	10
	237.9		a''					1						66	32		
	115.8		a''					2						33	64		
$F_j^\dagger$					4.84	10.90	4.71	2.75	0.51	0.51	1.05	0.60	1.66	2.27	0.069	0.007	0.72
uncertainty <sup>†</sup>					0.06	0.27	0.55	0.51	0.09	0.02	0.12	0.02	0.30	0.60	0.393	0.041	0.18

<sup>†</sup> Stretching force constants,  $\times 10^2$  N m<sup>-1</sup>; bending and bending interaction force constants,  $\times 10^{-18}$  N m;  
stretch-bending interaction force constants,  $\times 10^{-8}$  N.

1055-cm<sup>-1</sup> absorptions suggests that they might result from the occurrence of multiple trapping sites in the solid. Because the photolytic behavior of the 1049-cm<sup>-1</sup> peak was more definitely established than that of the 1055-cm<sup>-1</sup> peak and because this lower frequency peak falls closer to an observed gas-phase band center, it was chosen for use in the calculation.

Lippincott (3) assigned the prominent  $1004\text{-cm}^{-1}$  absorption to an  $a''$  fundamental and its companion at  $995\text{-cm}^{-1}$  to an  $a'$  fundamental of *cis*- $\text{CH}_3\text{ONO}$ . This calculation, for which the positions of the argon-matrix peaks have been used, reverses the assignment. Because of the small difference between these two absorption frequencies, the assignment is sensitive to a small change in the potential constants. The  $a'$  vibration is highly delocalized and cannot be simply correlated with a vibration of *cis*- $\text{CD}_3\text{ONO}$ . However, the  $a''$  vibration calculated to lie at  $988\text{-cm}^{-1}$  for *cis*- $\text{CH}_3\text{ONO}$  shifts to  $754\text{-cm}^{-1}$  for *cis*- $\text{CD}_3\text{ONO}$ . No absorption appeared near  $754\text{-cm}^{-1}$  in spectra of  $\text{CD}_3\text{ONO}$  isolated in solid argon, but the correction to  $995\text{-cm}^{-1}$  would shift the corresponding fundamental of the deuterated molecule to about  $760\text{-cm}^{-1}$ , on the low-frequency shoulder of the very prominent  $777\text{-cm}^{-1}$  absorption of *trans*- $\text{CD}_3\text{ONO}$ .

In contrast to the results of the force constant fit for *trans*- $\text{CH}_3\text{ONO}$ , the force constants related to motions of the inplane H atom of *cis*- $\text{CH}_3\text{ONO}$ , summarized in Table VI, are significantly different in magnitude from their counterparts related to motions of the out-of-plane H atoms. The statistical uncertainties in the CO- and N-O-stretching and ONO-bending force constants and in the interaction constants of the *cis* rotamer are large. Nevertheless, small changes in the initial set of force constants did not significantly affect the results of the calculation. In part, these uncertainties reflect the large amount of mixing of these three types of vibration. In the calculation of Bauer (8), the contribution of the ONO bending motion to the  $838\text{-cm}^{-1}$  vibration of *cis*- $\text{CH}_3\text{ONO}$  exceeded that of the N-O stretching motion. The reverse was true for the  $624\text{-cm}^{-1}$  vibration. In the present calculation, the  $838\text{-cm}^{-1}$  vibration had more N-O-stretching character than ONO-bending character, and the  $624\text{-cm}^{-1}$  vibration resulted predominantly from bending motions. On the basis of the assignments for *cis*-HONO (18) and for *trans*- $\text{CH}_3\text{ONO}$ , the assignment of the lower frequency to the ONO-bending vibration seems preferable. Evidence for a significant contribution of CO-stretching motion to the  $838\text{-cm}^{-1}$  vibration is provided by its relatively low intensity compared to the  $812\text{-cm}^{-1}$  absorption of *trans*- $\text{CH}_3\text{ONO}$ . In the *trans* molecule, the CO-stretching motion is concentrated in the moderately intense  $1046\text{-cm}^{-1}$  vibration, whereas the very strong  $812\text{-cm}^{-1}$  absorption results principally from N-O-stretching and ONO-bending motions. Mixing of CO-stretching motion into the  $838\text{-cm}^{-1}$  vibration of *cis*- $\text{CH}_3\text{ONO}$  would, therefore, be expected to diminish its absorption intensity, as is observed. The shift calculated for both the  $838\text{-cm}^{-1}$  and the  $624\text{-cm}^{-1}$  fundamentals on deuterium substitution is significantly greater than is observed, indicating that the contribution of hydrogen-deformation motions to both of these vibrations is somewhat overestimated in the calculation. The large statistical uncertainties for the two torsional constants result from the lack of sufficient isotopic data to fix the assignments to the individual torsional modes.

#### CONCLUSIONS

The vibrational spectra of the *cis* and *trans* rotamers of methyl and methyl- $d_3$  nitrite have been assigned. For both molecules a reasonable fit to the observed frequencies has been obtained using a relatively simple set of valence force potential constants. The potential function calculated for the *cis* rotamer suggests a high degree of mixing for the vibrational motions below  $1000\text{-cm}^{-1}$  and shows significant



differences between the potential constants involving deformation of the in-plane H atom and their counterparts for the out-of-plane H atoms, consistent with the occurrence of nonbonded H-atom interactions for this structure.

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